RAW MATERIALS

UDC 666.32:691.43

USE OF "BLUE CLAY" FROM THE MALOARKHANGEL'SKOE DEPOSIT IN THE PRODUCTION OF CERAMIC TILES

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Translated from Steklo i Keramika, No. 2, pp. 27 – 28, February, 2006.

The mineralogical composition and technological properties of "blue clay" from the Maloarkhangel'skoe deposit are studied. The possibility of using it in the production of ceramic tiles is considered.

Clays from the Maloarkhangel'skoe deposit are traditionally used in mixtures for producing ceramic tiles. This deposit is part of the lower Cretaceous sedimentation layer. The thickness of the productive layer varies from 4 to 6 m. The clays are represented by kaolinite-illite varieties with a high content of iron hydroxides [1]. The lower part of the layer in the interval of 6 – 9 m contains so-called "blue clay" with a high content of an organic component, whose application in the production of ceramic tiles is problematic.

The purpose of our study is to investigate the mineralogical composition and technological properties of "blue clay" and to estimate the possibility of using it in the production of ceramic tiles.

The peculiar blue tint of this clay in natural conditions is related to the presence of organic materials, which upon oxidation in air change to a gray tint. The considered clay has medium plasticity (plastic number 21 – 24) and a rather high binding capacity According to its content of Al_2O_3, it is classified as acid clay with a high content of colorant oxides. The amount of Fe_2O_3 in this clay varies from 5.6 to 7.0 wt.% (Table 1). The ratio $Fe_2O_3 : R_2O$ is 3.11 – 3.95 and the RO content does not exceed 1.8%.

The mineralogical composition has been studied using x-ray phase and differential-thermal analysis. The argillaceous minerals are kaolinite (30 – 35%) and illite (8 – 10%). The clay to a large extent is sand-contaminated and contains up to 30 – 40% quartz. Iron-bearing minerals are represented by goethite $Fe(OH)_2$ and to a lower extent jarosite $KFe^{3+}[(OH)_6(SO_4)_2]$.

According to its content of finely dispersed fractions, the clay can be attributed to the medium-dispersion group. It has medium sinterability, and its calcination loss varies from 9.5 to 11.0%.

Experimental mixtures were prepared using the slip technology. Initial components were milled to a residue of 2 – 4% on a No. 0063 sieve. The moisture of molding powder was 5 – 6%, and the granule size was below 0.63 mm. Samples were produced on a hydraulic press under a unit molding pressure of 32 and 24 MPa and dried at temperatures of 250 – 300°C to a residual moisture below 0.5%. Firing of samples was carried out in a temperature interval of 1100 – 1180°C. The heating rate varied within the limits of 6 – 34 K/min.

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TABLE 1

Clay sample	Depth of occurrence, m	Weight content, %*							$Fe_2O_3 : R_2O$
		SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	calcination loss	
1	6 – 7	54.80	20.80	0.60	0.90	6.20	0.09	10.50	3.44
2	7 – 8	56.40	21.90	0.50	0.90	7.00	0.07	9.50	3.95
3	8 – 9	53.60	22.30	0.50	0.80	5.60	0.10	10.20	3.11

* All samples contained 1.00% TiO_2 and 1.70% K_2O.

TABLE 2

Clay sample	Firing for 34 min at 1160°C		Firing for 42 min at 1180°C	
	water absorption, %	width, mm, and characteristics of central zone	water absorption, %	width, mm, and characteristics of central zone
1	Swelling	7.0, black	2.21	2.0, black
2	The same	8.5, black	2.58	4.0, black
3	2.39, weak swelling	8.0, dark gray	2.24	6.5, dark gray

Under fast firing conditions (heating rate 30 – 34 K/min) the considered clay is prone to the formation of a black core, deformation, and swelling (Fig. 1). Under heat treatment for 34 min practically all samples swelled. As the firing duration increased, the propensity for swelling decreased. This was also observed as the Fe_2O_3 content decreases. The width of the black core in fired samples varied depending on the clay composition and firing conditions. The maximum width of the black core was observed in samples made of clay with the highest content of Fe_2O_3 (occurrence depth 7 – 8 m). As the firing duration increased, the width of the black core decreased. This is typical of all considered clays. Thus, for 34 min firing duration the width of the black core depending on the clay composition was equal to 7.0 – 8.5 mm (sample thickness 10 mm); as the firing duration extended to 42 min, the black core width decreased to 2.0 – 6.5 mm (Table 2). After firing for 3 h the fired samples did not have a black core.

The propensity for the formation of a black core and swelling is related to the presence of organic compounds in clays, as well as a high content of Fe_2O_3 (5.6 – 7.0%) and is caused by the reduction of ferric oxides under fast firing by unburned carbon.

The x-ray phase analysis of samples fired according to the fast regime indicates that the external zones of heat-treated samples that are formed in oxidizing conditions have at least 8 – 10% hematite. The presence of the latter is confirmed by the reflections on the diffraction patterns with d/n = 0.3670, 0.2690, 0.2510, and 0.2210 nm. Among iron-bearing compounds, the prevalent one in the black core (inner zones) is wustite FeO (d/n = 0.2476, 0.2139, and 0.1553 nm) and, in a smaller quantity, magnetite Fe_3O_4 (d/n = 0.2955, 0.2550, 0.2100, and 0.1714 nm). At the same time, the start of a melting process with the formation of a silica-bearing matrix is registered in the inner part of the sample.

A number of authors [2, 3] have established that in order to prevent the reduction of iron oxides under fast firing, an exposure at 850 – 950°C is required, whose duration depends on the chemicomineralogical composition of the particular clay. The authors believe that an effective method is introducing chamotte as a grog components and a 5% chalk additive into the mixture.

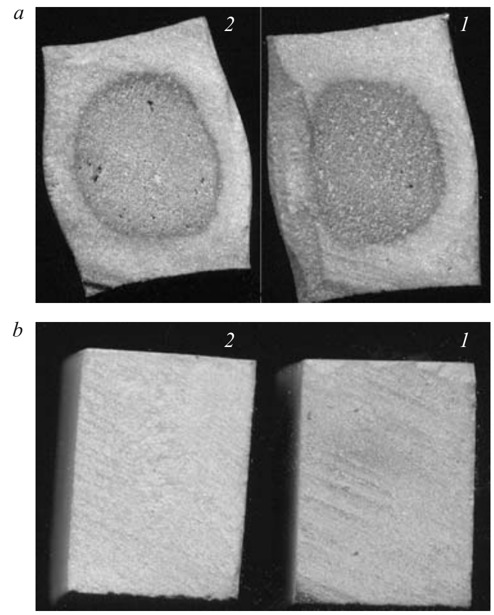

Fig. 1. Clay samples from bedding depth of 6 – 7 m (*1*) and 7 – 8 m (*2*) heat-treated with a heating rate of 30 – 34 K/min (*a*) and 6 – 7 K/min (*b*).

On firing with a heating rate not higher than 6 – 7 K/min (total heat treatment duration 3.0 – 3.5 h), samples made of the considered clays sinter well, without formation of defects. Their water absorption depending on their bedding depth varies from 7.6 – 9.7 to 1.1 – 2.7% under firing temperatures of 1100 and 1180°C, respectively. The fired samples have good strength parameters, The bending strength depending on the firing temperature and the depth of clay occurrence varies within the limits of 38 – 50 MPa. The sintering of the clay improves with increasing depth of occurrence.

Thus, clay from the lower levels of the Maloarkhangel’skoe deposit can be recommended for producing high-quality ceramic floor tiles under fast firing only as an additive mixed with clay from the upper levels. The heat treatment schedule should include an exposure for at least 10 min at 900°C.

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